Supplementary Material (SM)

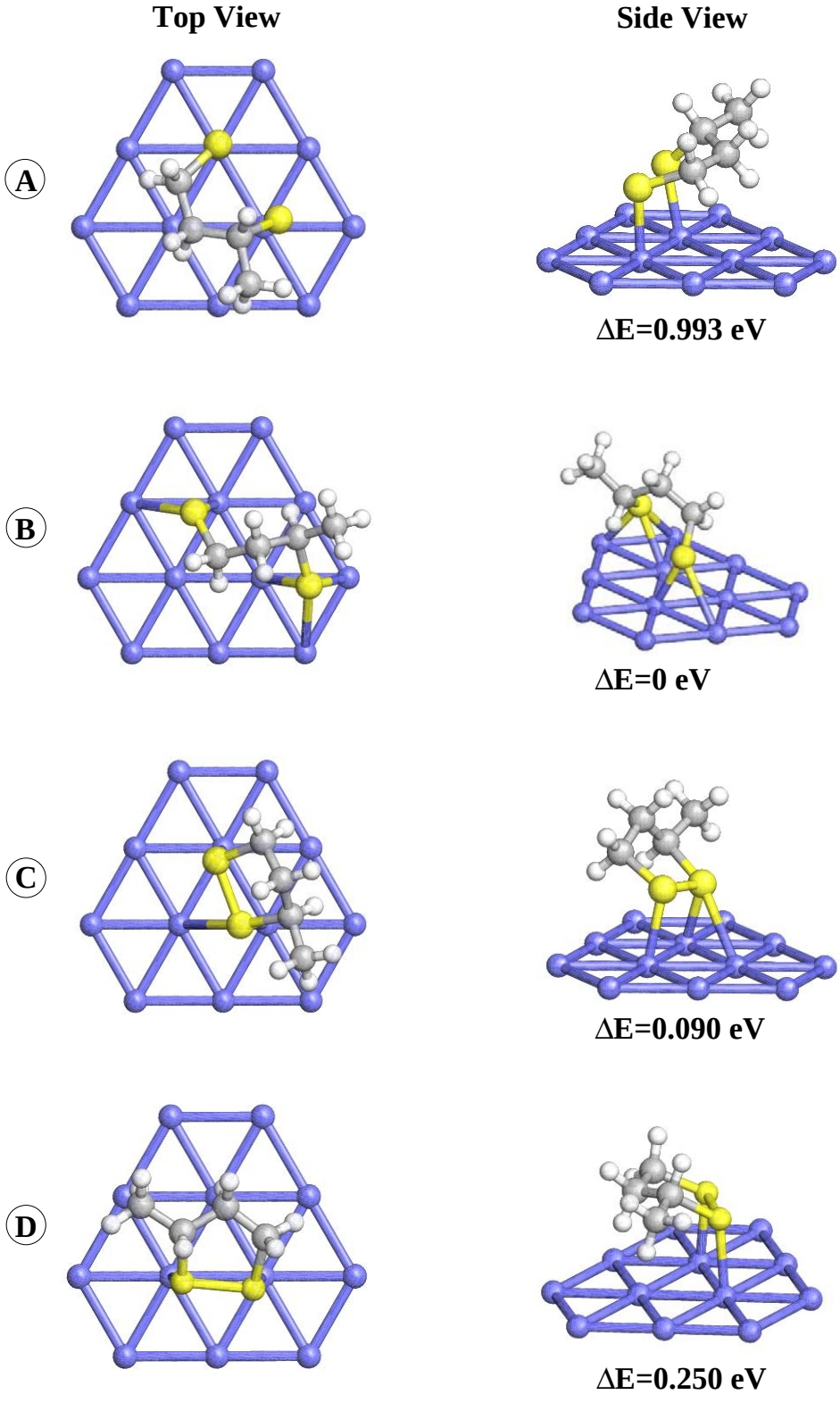
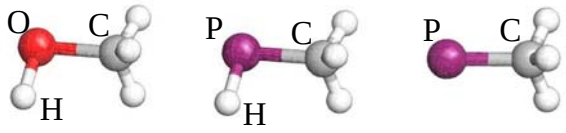
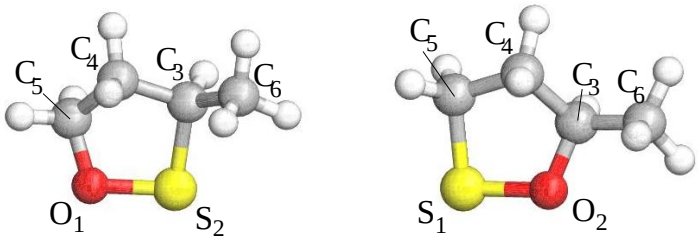


Figure 1: Structures of the calculated configurations for 3-Methyl-1,2-Dithiolane on a Pt_{12} cluster. In addition, the difference in total energy with respect to the most stable structure (B) is given.

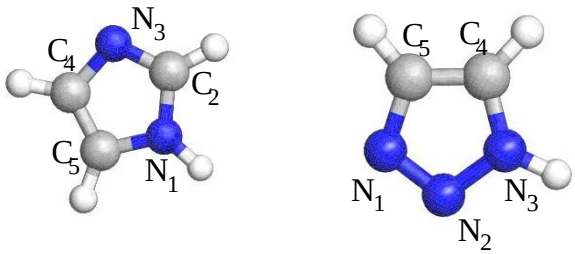
Methanol **Methyl−Phosphino** **Methanol**



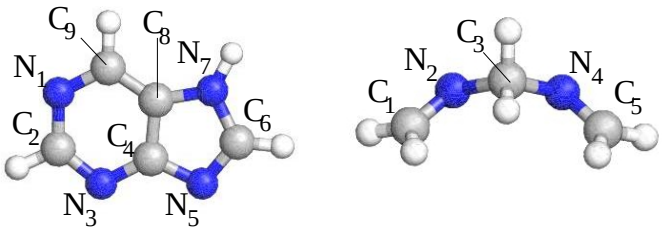
3−Methyl−1,2−Oxathiolane **3−Methyl−2,1−Oxathiolane**



Imidazole **1,2,3−Triazole**



Purine **2,4−Diazapentane**



3−Methyl−1,2−Diphospholane

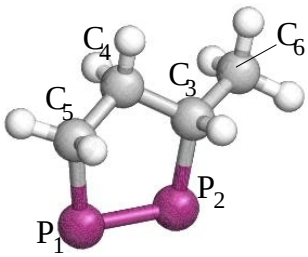


Figure 2: Different compounds studied as alternative alligator-clip molecule.

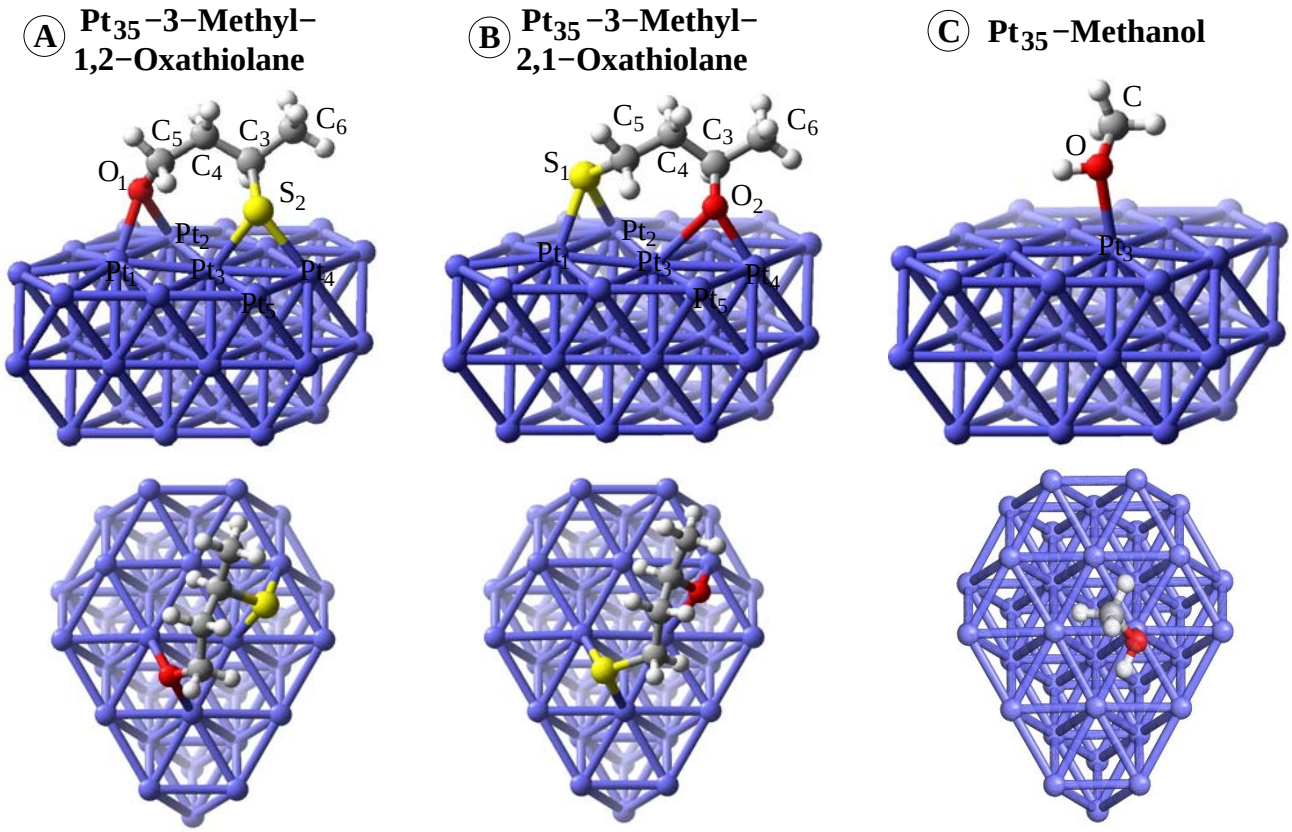


Figure 3: Optimized structures (on the Pt_{35} cluster) for some of the studied compounds.

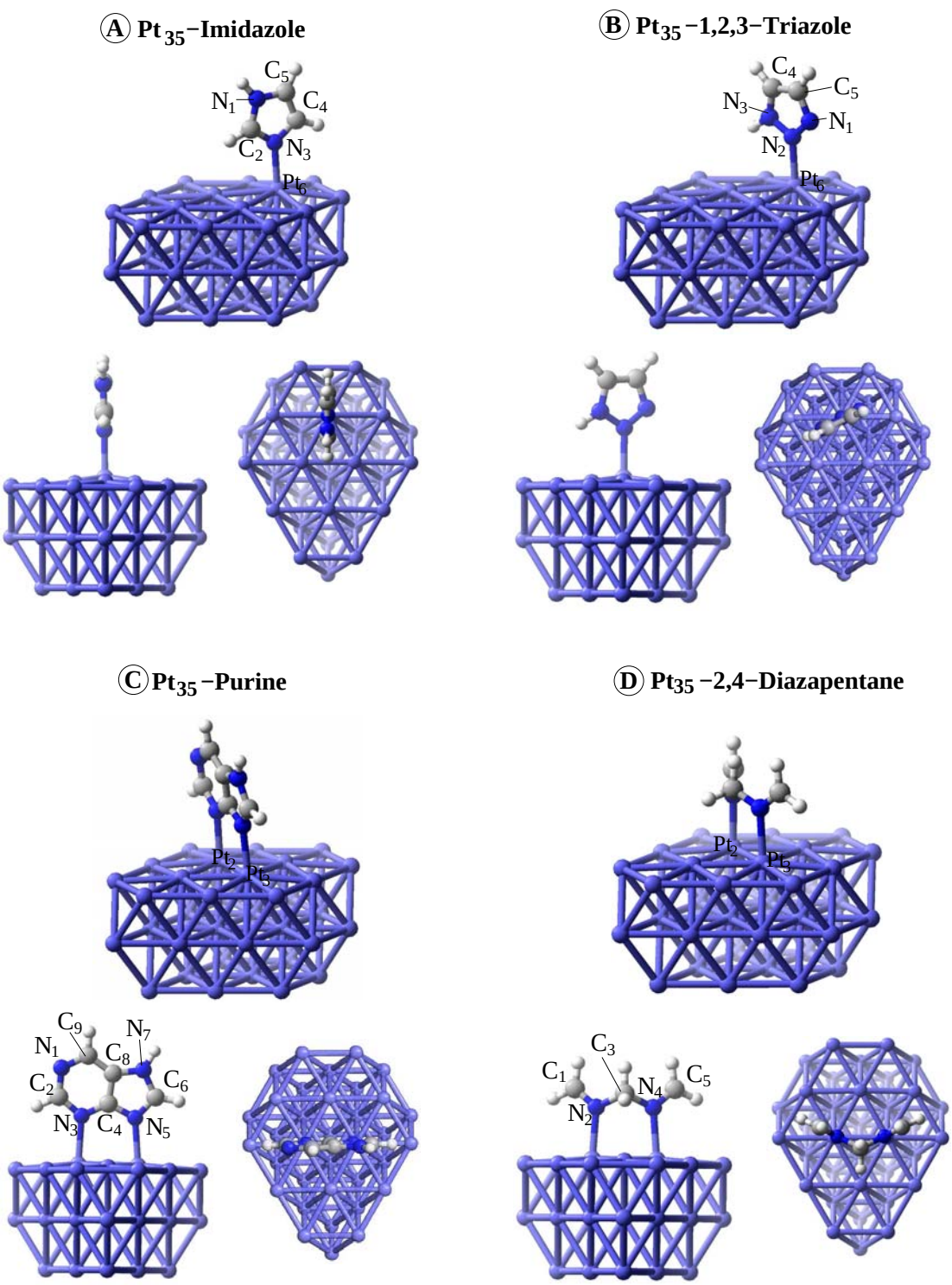


Figure 4: Optimized structures (on the Pt_{35} cluster) for all studied N-based compounds.

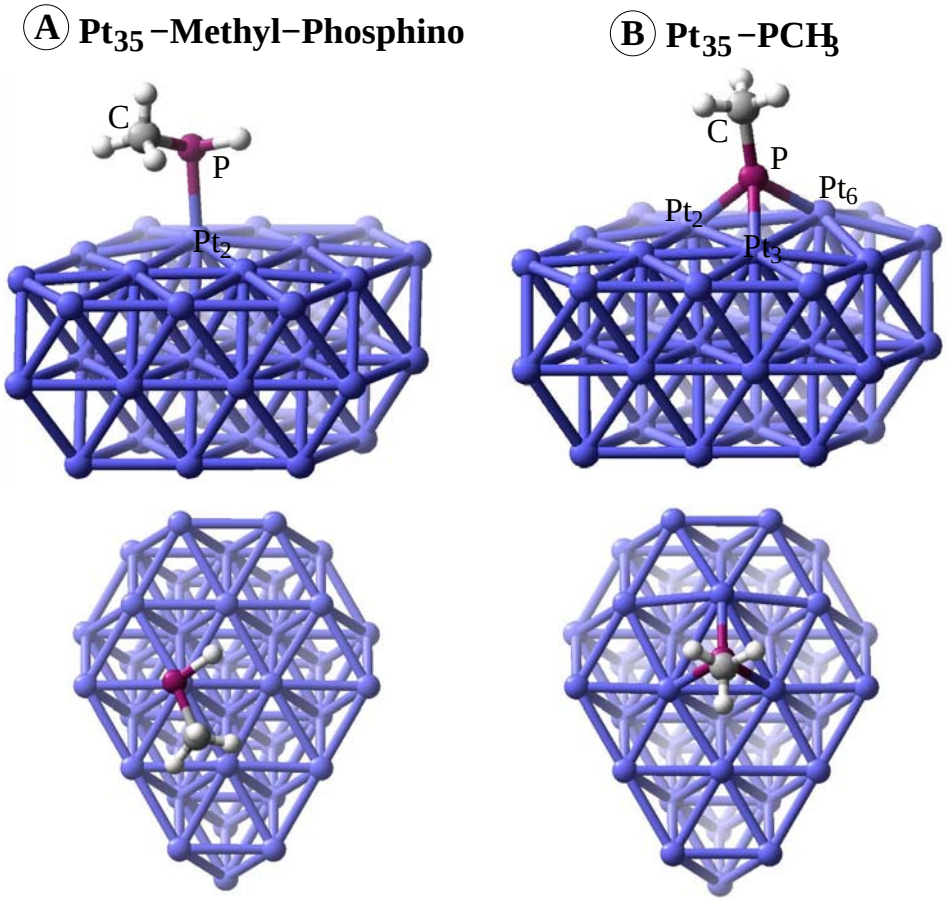


Figure 5: Optimized structures (on the Pt_{35} cluster) for all studied P-based compounds.

System	Spin-state	E_{tot} [h]	Distances [Å]	Angles [°]
Pt_{35}	11	-4171.575 5		
3-Methyl-1,2-Dithiolane	0	-953.624 6	C_5-S_1=1.848 S_1-S_2=2.149 S_2-C_3=1.856 C_3-C_4=1.531 C_3-C_6=1.527	C_5-S_1-S_2=95.1 S_1-S_2-C_3=95.5 S_2-C_3-C_4=107.0 C_3-C_4-C_5=109.4 C_4-C_5-S_1=108.7 S_2-C_3-C_6=109.6
3-Methyl-1,2-Diphospholane	0	-841.150 9	C_5-P_1=1.908 P_1-P_2=2.275 P_2-C_3=1.900 C_3-C_4=1.536 C_3-C_6=1.532	C_5-P_1-P_2=93.0 P_1-P_2-C_3=93.5 P_2-C_3-C_4=105.4 C_3-C_4-C_5=110.9 C_4-C_5-P_1=110.8 P_2-C_3-C_6=111.9
Methanol	0	-115.721 9	O-C=1.417	H-O-C=107.8
Methyl-Phosphino	½	-381.826 8	P-C=1.868	H-P-C=95.4
PCH_3	1	-381.200 7	P-C=1.861	P-C-H=110.7
3-Methyl-1,2-Oxathiolane	0	-630.623 6	C_5-O_1=1.426 O_1-S_2=1.724 S_2-C_3=1.861	C_5-O_1-S_2=108.2 O_1-S_2-C_3=94.9 S_2-C_3-C_4=102.8 C_3-C_4-C_5=106.2 C_4-C_5-O_1=106.6
3-Methyl-2,1-Oxathiolane	0	-630.628 3	C_5-S_1=1.848 S_1-O_2=1.722 O_2-C_3=1.431	C_5-S_1-O_2=94.4 S_1-O_2-C_3=109.4 O_2-C_3-C_4=105.7 C_3-C_4-C_5=106.2 C_4-C_5-S_1=103.6
Imidazole	0	-226.215 2	N_1-C_2=1.366 C_2-N_3=1.314 N_3-C_4=1.376 C_4-C_5=1.373 C_5-N_1=1.378	C_5-N_1-C_2=107.2 N_1-C_2-N_3=111.8 C_2-N_3-C_4=105.3 N_3-C_4-C_5=110.7 C_4-C_5-N_1=105.0
1,2,3-Triazole	0	-242.222 0	N_1-N_2=1.303 N_2-N_3=1.351 N_3-C_4=1.357 C_4-C_5=1.376 C_5-N_1=1.366	C_5-N_1-N_2=109.3 N_1-N_2-N_3=106.9 N_2-N_3-C_4=111.6 N_3-C_4-C_5=103.5 C_4-C_5-N_1=108.7
Purine	0	-411.930 8	N_1-C_2=1.347 C_2-N_3=1.334 N_3-C_4=1.334 C_4-C_8=1.419 C_4-N_5=1.380	N_1-C_2-N_3=128.1 C_2-N_3-C_4=114.1 N_3-C_4-C_8=122.3 C_4-N_5-C_6=104.4 C_6-N_7-C_8=106.2
2,4-Diazapentane	0	-227.372 0	$C_{1/5}$-$N_{2/4}$=1.267 $N_{2/4}$-C_3=1.456	$C_{1/5}$-$N_{2/4}$-C_3=117.0 N_2-C_3-N_4=109.8
3-Methyl-1,2-Diphospholane (H dissociated)	0	-839.943 0	C_5-P_1=1.894 P_1-P_2=2.046 P_2-C_3=1.905 C_3-C_4=1.534 C_3-C_6=1.532	C_5-P_1-P_2=96.9 P_1-P_2-C_3=97.3 P_2-C_3-C_4=108.3 C_3-C_4-C_5=110.4 C_4-C_5-P_1=109.6 P_2-C_3-C_6=112.8

Table 1: Ground spin-state and total energies for the different compounds in gas-phase. In addition, important distances and angles are given (for labels see Figure 3 in manuscript and Figure 2 in supplementary material).

System	Spin-state	E_{bind} [kcal/mol]	Distances [Å]	Angles [°]	Q(ads.) [e]
Pt_{35}	11	—	—	—	—
Pt_{35}-3-Methyl-1,2-Oxathiolane (SM-Fig. 3 A)	11	11.96 8	C_5-O_1=1.426 S_2-C_3=1.890 C_3-C_4=1.543 C_4-C_5=1.536 C_3-C_6=1.522 O_1-$Pt_{1/2}$=2.250 S_2-Pt_3=2.387 S_2-Pt_4=2.411	S_2-C_3-C_4=110.7 C_3-C_4-C_5=120.5 C_4-C_5-O_1=117.1 C_4-C_3-C_6=112.4 S_2-C_3-C_6=109.8 O_1-Pt_1-Pt_2-Pt_3=99.7 S_2-Pt_3-Pt_4-Pt_5=81.9	+0.369
Pt_{35}-3-Methyl-2,1-Oxathiolane (SM-Fig. 3 B)	11	11.43 7	C_5-S_1=1.875 O_2-C_3=1.421 C_3-C_4=1.543 C_4-C_5=1.532 C_3-C_6=1.523 S_1-$Pt_{1/2}$=2.420 O_2-Pt_3=2.500 O_2-Pt_4=2.076	O_2-C_3-C_4=107.8 C_3-C_4-C_5=117.5 C_4-C_5-S_1=117.1 C_4-C_3-C_6=112.3 O_2-C_3-C_6=112.2 S_1-Pt_1-Pt_2-Pt_3=99.8 O_2-Pt_3-Pt_4-Pt_5=95.1	+0.350
Pt_{35}-Methanol (SM-Fig. 3 C)	11	11.71 7	O-C=1.442 O-Pt_3=2.378	H-C-H=109.7 H-O-C=108.9 Pt_3-O-C=119.4	+0.284
Pt_{35}-Imidazole (SM-Fig. 4 A)	11	26.50 3	N_1-C_2=1.352 C_2-N_3=1.327 N_3-C_4=1.381 C_4-C_5=1.367 C_5-N_1=1.381 Pt_6-N_3=2.117	C_5-N_1-C_2=108.7 N_1-C_2-N_3=109.3 C_2-N_3-C_4=107.6 N_3-C_4-C_5=108.7 C_4-C_5-N_1=105.8 $S^{\perp}$-Molecule=0.5	+0.342
Pt_{35}-1,2,3-Triazole (SM-Fig. 4 B)	11	17.75 9	N_1-N_2=1.298 N_2-N_3=1.342 N_3-C_4=1.349 C_4-C_5=1.391 C_5-N_1=1.357 N_2-Pt_6=2.136	C_5-N_1-N_2=108.0 N_1-N_2-N_3=109.0 N_2-N_3-C_4=110.0 N_3-C_4-C_5=104.2 C_4-C_5-N_1=108.9 $S^{\perp}$-Molecule=5.1	+0.235
Pt_{35}-Purine (SM-Fig. 4 C)	11	24.73 5	N_1-C_2=1.338 C_2-N_3=1.343 N_3-C_4=1.336 C_4-C_8=1.405 C_8-C_9=1.390 N_3-N_5=2.427 N_3-Pt_2=2.210 N_5-Pt_3=2.178 Pt_2-Pt_3=2.702	N_1-C_2-N_3=125.7 C_2-N_3-C_4=115.0 N_3-C_4-C_8=122.8 C_4-N_5-C_6=106.0 C_6-N_7-C_8=107.3 N_7-C_8-C_9=137.1 Pt_2-Pt_3-N_5=85.3 Pt_3-Pt_2-N_3=87.5 $S^{\perp}$-Molecule=8.7	+0.433
Pt_{35}-2,4-Diazapentane (SM-Fig. 4 D)	12	24.74 4	$C_{1/5}$-$N_{2/4}$=1.275 $N_{2/4}$-C_3=1.463 N_2-Pt_2=2.213 N_4-Pt_3=2.219 Pt_2-Pt_3=2.714	$C_{1/5}$-$N_{2/4}$-C_3=118.5 N_2-C_3-N_4=110.5 $Pt_{2/3}$-$N_{2/4}$-C_3=117.0 Pt_2-Pt_3-N_4=85.8 Pt_3-Pt_2-N_2=86.2	+0.547
Pt_{35}-Methyl-Phosphino (SM-Fig. 5 A)	$^{21}/_2$	44.68 6	P-C=1.862 P-Pt_2=2.314	H-C-H=108.8 H-P-C=96.7 Pt_2-P-C=108.6	+0.429
Pt_{35}-PCH_3 (SM-Fig. 5 B)	10	92.93 0	C-P=1.826 $Pt_{2/3}$-P=2.237 Pt_6-P=2.219	H-C-H=110.1 H-P-C=108.7 $Pt_{2/3}$-P-C=124.8 Pt_6-P-C=130.3	+0.598

Table 2: Ground spin-state and binding energies for all compounds except MDTL and MDPL. In addition, important distances and angles are given (for labels see Figures 3-5 in supplementary material).